

Investigating bioalteration products on seafloor basalts, Fe sulfides and Fe oxyhydroxides using scanning transmission X-ray microscopy (STXM) and absorption spectroscopy

AMANDA G. HADDAD^{1*}, COLLEEN L. HOFFMAN¹, FRIEDER KLEIN², SARAH A. BENNETT^{1,3}, ROMAN A. BARCO¹ AND KATRINA J. EDWARDS¹

¹University of Southern California, Los Angeles, USA,
agturner@usc.edu (* presenting author)

²Woods Hole Oceanographic Institution, Woods Hole, USA,
fklein@whoi.edu

³NASA Jet Propulsion Laboratory, Pasadena, USA,
sarah.a.bennett@jpl.nasa.gov

Section Heading

Seafloor hydrothermal vent chimneys and the basaltic ocean crust are chemically reduced at the time of their formation but quickly undergo alteration following exposure to the oxygenated seawater. Alteration reactions (namely Fe and S oxidation and hydration) begin immediately at the rock-seawater interface yet when occurring abiotically, these reactions are kinetically inhibited, occurring very slowly if at all. It is suggested that microbes influence, if not control, these low-temperature alteration reactions at the rock-seawater interface in order to fix an estimated $\sim 1 \times 10^{19}$ g C per year [1]. In doing so, they influence global cycling of C, Fe, Mn, S and many other biogeochemically salient elements [2].

Understanding seafloor microbe-mineral interactions requires that we characterize how the minerals are changing as a result of being colonized by microbes. To investigate bioalteration products of seafloor microbe-mineral interactions, polished panels of common seafloor substrates (basalts, Fe sulfides, Fe oxyhydroxides) were allowed to react with in situ bottom water on the flanks of the Lo'ihi Seamount, Hawai'i for up to three years. After reaction, these panels developed thin (micron-scale) veneers of secondary alteration products and have been shown to harbor microbes found on seafloor basalts and hydrothermal sulfides (Haddad, unpub. data). We examined the products for morphology via scanning transmission X-ray microscopy (STXM) and changes in chemistry and mineralogy via C K-, Fe K- and O K-edge near edge X-ray absorption fine structure (NEXAFS). The alteration products on the reacted panels are amorphous Fe(III) and short-range Fe(III) mineraloids similar to those found on seafloor basalts. We present the range in chemistry and particle morphologies observed and discuss the variability with mineralogy.

[1] Bach (2003) *Geochim Cosmochim Acta* **67**, 3871-3887.

[2] Orcutt (2011) *Microbio Mol Bio Rev* **75**, 361-422.

Modeling the dioctahedral smectites CEC variation versus structural Iron reduction level

J. HADI^{1*}, C. TOURNASSAT¹, I. IGNATIADIS¹, L. CHARLET²

¹BRGM, Avenue Claude Guillemin, BP 36009, 45060 Orléans, Cedex 2, France

²ISTERRE, BP 53, 38041 Grenoble, Cedex

Abstract

Iron is one of the most common redox species in soils and sedimentary rocks. Amongst iron-bearing phases, phyllosilicates might play key roles in various bio-geochemical processes involving redox reactions, where structural Fe (Festr) acts as a renewable source/trap of electron. A large set of data from kinetics, spectroscopic or electrochemical studies on dioctahedral smectites demonstrate that reduction of Festr impacts many clay properties such as colour, layer charge, swelling pressure, and colloidal properties that are linked to layer structural changes. Experiments also suggest that this mechanism is partly reversible, depending on type and properties of the primary oxidized clay and on extent of iron reduction level. The complexity of the involved mechanisms makes the prediction of Festr redox properties challenging. For instance, only empirical models are currently available to quantify structural changes as a function of reduction level. However, a predictive and mechanistic model of these changes is a prerequisite to develop a thermodynamic model for Festr redox properties. In this contribution, we propose a mechanistic statistical model to explain 2:1 layer excess negative charge changes induced by chemical reduction (dithionite) of structural Fe(III) to Fe(II). This model completes this published by Drits and Manceau [1] and was calibrated on data from our own and from the literature.

[1] Drits, V. A. and Manceau A. (2000) *A model for the mechanism of Fe³⁺ to Fe²⁺ reduction in dioctahedral smectites*. *Clays and Clay Minerals* **48#**, 185-195.